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NONEQUILIBRIUM IONIZATION BEHIND A STRONG SHOCK WAVE IN THE MARS ATMOSPHERE

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The paper reports results of experimental and numerical studies of nonequilibrium ionization behind a strong shock wave in the Mars atmosphere. The calculated kinetic model is verified by measuring the electron concentrations and temperature in the relaxation zone

Introduction. The choice of an appropriate model for physicochemical transformations in a high-temperature gas mixture plays an important role in numerical simulations of nonequilibrium flow around spacecraft in hypersonic atmospheric flight. The kinetic processes in a multicomponent gas mixture consisting of atoms, molecules, ions, and electrons are very complex. At present, they can be taken into account only using a model description, which does not always adequately represent the processes occurring under flight conditions. In this connection, verification of kinetic and numerical models during experiments is very important.

In studies of the atmosphere of some solar system planets (for example, Mars), the challenge now is to describe the nonequilibrium physicochemical transformations in gas mixtures of complex composition. Because there are no reliable data on the physicochemical processes occurring in the Mars entry environment and because special flight experiments are not feasible, of importance are joint numerical and laboratory (on aerodynamic facilities) experiments on nonequilibrium thermophysical processes under conditions modeling the Mars entry parameters. The nonequilibrium flow around spacecraft flying in the Mars atmosphere has been extensively studied. For example, kinetic models for physicochemical transformations that have been used as the basis for investigations in this field are given in [1–3]. However, part of the data included in these models has not been verified and has the character of estimates.

In the present work, we attempted to correct a calculated kinetic model by comparing numerical and experimental data on the nonequilibrium ionization parameters behind a strong shock-wave front in a CO_2–N_2–O_2 mixture, which models the composition of the Mars atmosphere.

Experimental Studies of Nonequilibrium Ionization behind a Shock Wave in the Mars Atmosphere. The experiments were performed in the electric-discharge tube (EDT) at the Central Aerohydrodynamic Institute [4]. The EDT was used to study physicochemical processes behind strong shock waves propagating with velocities of 4–15 km/sec [5, 6]. The walls of the discharge tube are ceramic, and the electrodes are made of molybdenum. The propelling gas is helium heated by a powerful electric discharge. The low-pressure channel 5 m long and 57 mm in diameters consists of glass sections joined together by metallic flanges. The low-pressure channel was previously evacuated to a pressure of 0.13 Pa. The Mars atmosphere was modeled by a mixture of air and CO_2. The channel of the tube was filled with a mixture containing CO_2 (96%), N_2 (3%), and O_2 (1%). The difference between the mixture and the Mars atmosphere lies in

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the increased content of O_2 and the absence of Ar. Estimates show that variation in the concentration of O_2 and Ar within 0–3% ahead of the shock-wave front practically does not influence the postshock relaxation processes. Most of the experiments were performed at an initial channel pressure of $p_0 = (26.70 \pm 0.27)$ Pa. The shock-wave speed was measured with an error of 2%. At shock-wave speeds of $v_s = 4$–9 km/sec, the duration of "lock" was 3–7 μsec, which indicates that using the EDT, it is possible to study the processes in the nonequilibrium zone adjacent to the shock-wave front and in the narrow quasistationary zone. During the experiments, we measured distributions of the electron $n_{\rm e}$ and ion $n_{\rm i}$ concentrations and the electron temperature $T_{\rm e}$ in the relaxation zone behind the shock-wave front.

Measurements of the Charged-Particle Concentration. The ion and electron concentrations were measured using probes of various types. Single cylindrical probes were placed in parallel and normal to the flow and operated in the regime of ionic- and electron-current collection. The diameters of the probe electrodes were varied from 0.1 to 0.01 mm, depending on experimental conditions. Experimental data were processed using the results obtained in studies of probe operation in hypersonic flows behind a shock-wave front in the transition regime at Knudsen numbers of $0.1 \leqslant {\rm Kn} \leqslant 10$ (${\rm Kn} = \lambda_{\rm i,e}/r_p$, where $\lambda_{\rm i,e}$ is the free path for ions and electrons and r_p is the radius of the probe) [7]. For longitudinal cylindrical probes operating in the regime of electron and ion collection, the electron $J_{\rm e}$ and ionic $J_{\rm i}$ currents are related to $n_{\rm e}$ and $n_{\rm i}$ by the formula

$$J_{\rm e,i} = \bar{j}_{\rm e,i} S_p n_{\rm e,i} e (kT_{\rm e}/(2\pi m_{\rm e,i}))^{0.5}, \tag{1}$$

where e is the electron charge, $m_{\rm e}$ and $m_{\rm i}$ are the electron and ionic masses, respectively, k is the Boltzmann constant, S_p is the surface area of the probe electrode, and $\bar{j}_{\rm e,i}$ is the dimensionless current density under the probe operation conditions in the plasma studied, which is determined for the operation conditions in the EDT from the results of [5]. The use of a thin cylindrical probe located normal to the flow increases the spatial resolution of the probing. For the regime of a thin near-probe layer and ${\rm Kn} \geqslant 1$, we used the relation of [7] $J_{\rm i} = 2r_p l_p n_{\rm i} e u$ (l_p is the length of the probe electrode and u is the mass velocity of the gas, which is equal to the mass velocity of the ions $u_{\rm i}$). This makes it possible to determine $n_{\rm i}$ for known values of the velocity u and does not require information on the values of $T_{\rm e}$ and $m_{\rm i}$ (the calculation error for the indicated formula does not exceed 20%). Using a longitudinal cylindrical probe operating in the electron collection regime at ${\rm Kn} < 10$, we observed a strong dependence of $\bar{j}_{\rm e}$ on Kn. This dependence can be taken into account for a known (for example, calculated) free path of electrons. At the same time, $j_{\rm e}$ can be determined with the simultaneous use of two single probes of different diameters d_1 and d_2 [8]. In this case, for the characteristic conditions of the EDT, the approximation relation for the $\bar{j}_{\rm e}$ of the second probe can be obtained in the form $\bar{j}_{\rm e2} \simeq (1 - J_{\rm e1}/J_{\rm e2})/[(d_1/d_2 - 1)(J_{\rm e1}/J_{\rm e2})]$, where $J_{\rm e1}$ and $J_{\rm e2}$ are the currents measured by probes with diameters d_1 and d_2, respectively. For known values of $T_{\rm e}$, it is not difficult to evaluate the electron concentration from formula (1). In Fig. 1, the quasistationary electron concentration $n_{\rm e,q}$ (points 1 and 2) and ion concentration $n_{\rm i,q}$ (points 3 and 4) are plotted versus the shock-wave velocity for $p_0 = 26.7$ Pa. Points 1–4 correspond to measurements using longitudinal and transverse probes, two single probes, and a longitudinal probe using electron Knudsen numbers [8]. The electron concentration profile measured in the relaxation zone behind the shock-wave front is shown by points in Fig. 2 for $v_s = 4.15$ km/sec and $p_0 = 53.3$ Pa.

Electron Temperature Measurement. Measurement of $T_{\rm e}$ for shock-wave propagation along the tube channel, which is required to determine $n_{\rm e,i}$, is of independent interest because the electron temperature is an important parameter in determining the radiative characteristics of gases. The distribution of $T_{\rm e}$ can be used to verify numerical models for nonequilibrium processes (for example, vibrational relaxation of some molecules) for propagation of a strong shock wave in gases. To measure $T_{\rm e}$, we used the method of a triple probe [9] and the data of [5, 7]. A diagram of a triple probe is shown in Fig. 3. The electrodes are made of stainless steel and have the following dimensions: thickness 0.1 mm, $a = 5$ and 1 mm, and $b = 4$ and 7 mm. The interelectrode gap is $D = 4$ mm. The spatial resolution of the system along the flow-velocity vector is 0.5–1.0 mm. The time resolution of the measuring system is 0.1 μsec, which is much larger than the time required to form a near-probe layer of space charge (10^{-3} μsec). The approximation relation for determining $T_{\rm e}$ from the measured potential difference V_{d2} has the form

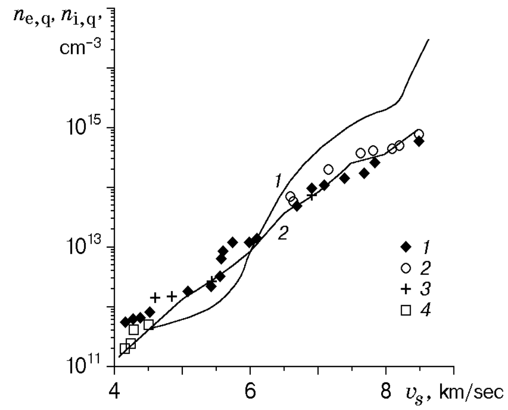

Fig. 1

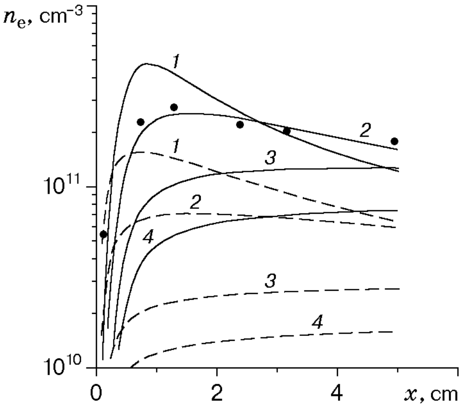

Fig. 2

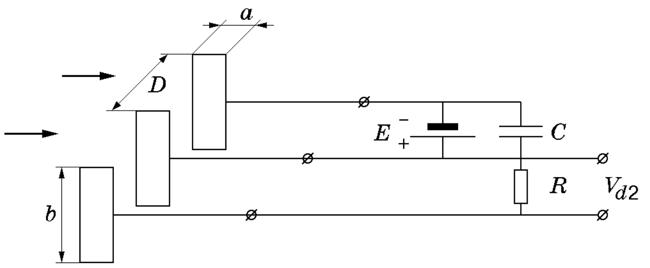

Fig. 3

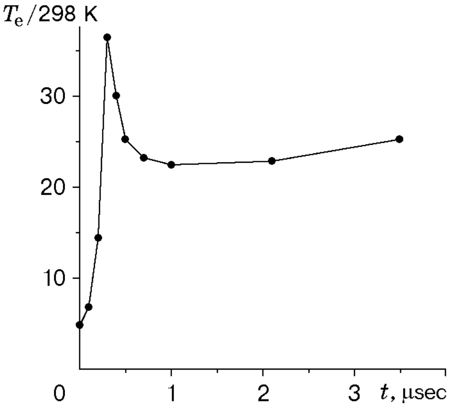

Fig. 4

$$T_e \approx V_{d2}e/[k\,\ln{(j_{i1}/j_{i3}+1)}], \tag{2}$$

provided that $\exp{(-eE/(kT_e))} \ll 1$, where E is the battery voltage. The ratio j_{i1}/j_{i3} is obtained by probe measurements to determine the features of probe operation in the ionic current saturation regime. As follows from (2), measurements of V_{d2} make it is possible to determine T_e and its distribution with time. In this case, it is necessary to satisfy the condition $R_{in} \gg 2kT_e/(ei_iS_p)$ (R_{in} is the input resistance of the apparatus and i_i is the density of the ionic current supplied to the probe electrode). Figure 4 gives the measured distribution of the electron temperature T_e in the relaxation zone for $v_s = 8.1$ km/sec and $p_0 = 26.7$ Pa. Immediately behind the shock-wave front, the T_e has a maximum. After that, the electron temperature decreases sharply in a relatively thin zone, reaching a minimum, and then increases monotonically to its quasiequilibrium value.

Numerical Simulation of Nonequilibrium Ionization behind a Shock-Wave in the Mars Atmosphere. The flow behind a strong shock wave was studied by numerical simulation in an inviscid quasistationary formulation. The shock-wave speed is in the range $v_s = 4$–9 km/sec. In this approximation, the mathematical model for the flow in the relaxation zone is a system of algebraic continuity, momentum, and energy equations, which is solved simultaneously with the differential equations describing the variations in the mixture composition (component concentrations), the vibrational energy of molecules, and the energy of free electrons. This system is solved using the standard integration program for large systems of "rigid" differential equations [10], which was specially developed for numerical simulation of nonequilibrium processes in gas-dynamic flows.

It is assumed the Mars atmosphere consists of CO_2 (97%) and N_2 (3%). At high temperatures, the gas mixture is modeled by a mixture of atomic and molecular gases (CO_2, CO, C_2, N_2, NO, O_2, CN, C, N, O, and Ar), ions (CO^+, C^+, O^+, O_2^+, and NO^+), and electrons. The rotational degrees of freedom are in thermodynamic equilibrium with the translational degrees. The vibrational degrees of freedom of CO_2, CO, C_2, N_2, NO, O_2, and CN molecules are in nonequilibrium excitation. The temperature of free electrons is assumed to be different from the translational and vibrational temperatures of the molecules.

As the initial model in the flow calculations we used the kinetic model of [1], which is a combination of the schemes of nonequilibrium physicochemical transformations from [2, 3]. The model of nonequilibrium processes was corrected for the three ionization parameters measured during the experiment in the EDT: the quasistationary value of the electron concentration $n_{\rm e,q}$, the time of attainment of peak electron concentrations $\tau_{\rm i,max}$, and the peak electron concentration $n_{\rm e,max}$. Test calculations showed that these parameters depend strongly on the relaxation time, reaction-rate constants, and kinetic models. This makes it possible to choose an adequate model for describing the nonequilibrium flow in the tested range of shock-wave speeds from a comparison of data of numerical and laboratory experiments. At the first stage, the ionization characteristics of the postshock flow in the Martian mixture for speeds $v_s = 4$–9 km/sec were calculated using the model of [1]. The dependence $n_{\rm e,q}(v_s)$ obtained from these test calculations is presented in Fig. 1 (curve 1). It is easy to see that there is a considerable difference between calculation results for the kinetic model of [1] and experimental data. This difference (which is especially large for speeds $v_s < 5$ km/sec and $v_s > 7$ km/sec) was used as the basis for correction of the model of physicochemical transformations.

Below, we give a scheme of nonequilibrium physicochemical processes that provides a best fit (curve 2 in Fig. 1) to the data from the EDT experiments on the ionization parameters in the tested speed range for a strong shock-wave in a CO_2–N_2 mixture.

It was assumed that the rotational degrees of freedom of the molecules are in equilibrium with the translational degrees of freedom, i.e., $T_r = T$.

In the calculation of the vibrational relaxation for CO_2, CO, CN, O_2, N_2, and C_2 molecules, it was assumed they exchange energy during the vibrational-translational (VT) processes and vibrational-dissociation interaction (VDI). For the excitation of CO and N_2 molecules at $v_s > 8$ km/sec, energy exchange with free electrons during the electron impact reaction becomes important. The vibrational-translational exchange $p\tau_{\rm VT}$ [atm · sec] was calculated from the Milliken–White formula [11]

$$p\tau_{\rm VT} = \exp\,[a(T^{-1/3} - b) - 18.42],$$

where $a = 0.001\,16\mu^{0.5}\theta^{1.333}$, $b = 0.015\mu^{0.25}$, p is the pressure, T is the translational temperature, μ is the reduced mass of the colliding particles, and θ is the characteristic vibrational temperature of the molecule. The nonphysical behavior of the relaxation time at high temperatures was corrected for all molecules by introducing the Park correction [2] $\tau_{\rm P} = (n_t\sqrt{8kT/(\pi m)}\,\sigma_V)^{-1}$, where n_t is the density of the colliding particles, m is the average mass of the gas particles, and $\sigma_V = \sigma'_V(50{,}000/T)^2$ is the collision cross section, where $\sigma'_V = 3\cdot 10^{-17}$ cm^2 for N_2, O_2, and NO, $3\cdot 10^{-18}$ cm^2 for CO, and 10^{-16} cm^2 for CO_2. With allowance for the Park correction, the VT relaxation time is calculated form the formula $\tau = \tau_{\rm VT} + \tau_{\rm P}$.

In the numerical model, the VDI was taken into account using the Kuznetsov model [12], which was generalized to the case of dissociation of a CO_2 molecule. The rate constant of molecule dissociation takes into account the nonequilibrium effect similarly to the CVDV model [13] by means of the factor $Z(T, T_V)$, which, for a CO_2 molecule, has the form

$$Z(T, T_V) = \Big(\prod_{j=1}^{m} Q_j(T)\Big/\prod_{j=1}^{m} Q_j(T_{Vj})\Big)\exp\Big[-E_V^*\Big(m\Big/\sum_{i=1}^{m} T_{Vi} - 1/T\Big)\Big],$$

where $Q_j(T_f) = (1 - \exp(-\theta_j/T_f))^{-dj}$ ($T_f = T$ or $T_f = T_{Vj}$).

For a CO_2 molecule, the coefficients have the following values: $m = 3$, $\theta_1 = 1903$ K, $d_1 = 1$, $\theta_2 = 945$ K, $d_2 = 2$, $\theta_3 = 3339$ K, $d_3 = 1$, and $E_V^* = 34{,}600$ K.

For diatomic molecules, the factor $Z(T, T_V)$ has the form

$$Z(T, T_V) = \frac{Q(T)}{Q(T_V)}\exp\Big[E_V^*\Big(\frac{1}{T} - \frac{1}{T_V}\Big)\Big], \qquad E_V^* = \frac{D}{2},$$

where D is the dissociation energy for the molecule.

We note that this model is one of the few VDI models that describe the effect of vibrational nonequilibrium on the dissociation of a multiatomic molecule, and hence, it is used in the refined kinetic model to allow for the vibrational-dissociation exchange.

In constructing the system of physicochemical processes, we used primarily the two well-known models [1, 2] for the kinetics of dissociation reactions and exchange processes. Our numerical experiment shows that a best fit to the measurements of ionization behind the shock-wave front at 4 km/sec $< v_s <$ 9 km/sec is provided for by the kinetic model in which the dissociation of CO_2 is described using the constant of the direct process k_d [$\mathrm{cm}^3/(\mathrm{mole} \cdot \mathrm{sec})$]. For Ar, this constant is equal to $k_d = (1.7 \cdot 10^{20})T^{-1.5} \exp(-63{,}275/T)$. The dissociation (recombination) of the diatomic molecules and exchange reactions were calculated according to the data of [1]. The kinetics of the exchange reaction of NO formation corresponds to the Zel'dovich scheme using the two-temperature reaction-rate constants proposed in [14].

The ionization in the relaxation zone behind a shock-wave front in the speed range studied is described by the reactions of associative ionization and ionization of atoms by electron impact. Under these conditions, the main process of electron formation is associative ionization with formation of NO^+ ions. Variation of the rate constants for associative ionization proposed in [1, 15, 16] shows that the ionization processes depend strongly on the choice of values for the constants. Therefore, in the present paper, considerable attention was given to the improvement of accuracy in measuring n_{i} and n_{e}, especially in the range of relatively low shock-wave speeds ($v_s <$ 5 km/sec), where there is a marked difference between measurements and results of calculation of n_{e} using the conventional models.

Figure 2 illustrates the effect of the choice of a kinetic model for associative ionization on the profiles of $n_{\mathrm{e}} = n_{\mathrm{e}}(x)$ for $v_s =$ 4.15 km/sec and $p_0 =$ 53.3 Pa. Curves 1–4 correspond to the $n_{\mathrm{e}}(x)$ calculated using the associative ionization rate constants from [1, 3, 15, 16]. The solid curves were obtained for CO_2 dissociation using the rate constant proposed in the present paper. The dashed curves correspond to a calculation for the model of CO_2 dissociation from [1]. From Fig. 2 it can be seen that ionization is well described by the kinetics of [3] (curve 2). Reaction-rate constants for the ionization of C and O atoms by electron impact are given in [2]. The inclusion of these reaction in the kinetic model does not affect the ionization at $v_s <$ 8 km/sec and leads to an increase in $n_{\mathrm{e,q}}$ at $v_s \geqslant$ 8 km/sec.

The resonantly fast reactions of charge exchange between neutral and positively charged atoms and molecules play an important role in the formation of the ionized components of the high-temperature mixture. Kinetic data for the rates of charge-exchange reactions are insufficient. The model includes the charge-exchange reactions given in [2]. Test calculations and a comparison with measured electron densities indicate that the basic system adequately describes the charge-exchange reactions, except for the reactions $O_2 + C^+ = O_2^+ + C$ and $CO + C^+ = CO^+ + C$, whose rate constants given in [2] are apparently overestimated. In the present kinetic model they are decreased by a factor of 10.

The temperature of free electrons is determined from the energy balance of the electron gas [17]. It is assumed that the electrons lose (acquire) energy in elastic and inelastic collisions with the neutral and charged heavy components of the plasma.

The associative ionization reactions produce "hot" electrons with a temperature of the order of the translational temperature of the gas [18].

The presence of high concentrations of N_2 and CO molecules in the mixture leads to the necessity of taking into account the loss of electron energy in the reactions of electron-vibrational (EV) exchange $N_2(v) + e = N_2(v') + e$ and $CO(v) + e = CO(v') + e$ (v and v' are the numbers of vibrational levels of the ground electron state), which proceed at resonantly high rates via the formation of unstable negative ions N_2^- and CO^- [19]. The distribution of T_{e} in the relaxation zone is largely determined by the EV processes [17]. In addition, the energy-balance equation for the electron gas takes into account the rates of loss of electron energy due to the ionization and excitation of metastable electron states of molecules and atoms by electron impact, excitation of rotational degrees of freedom, and dissociation of molecules of the mixture in collisions with electrons.

Figure 5 gives calculated distributions of the temperature T, vibrational temperatures T_{v,N_2} and $T_{v,CO}$ of N_2 and CO molecules, and electron temperature T_{e} in the relaxation zone (curves 1–4, respectively) for $v_s =$ 7 km/sec and $p_0 =$ 26.7 Pa. The qualitative nature of the calculated distribution of T_{e} and the

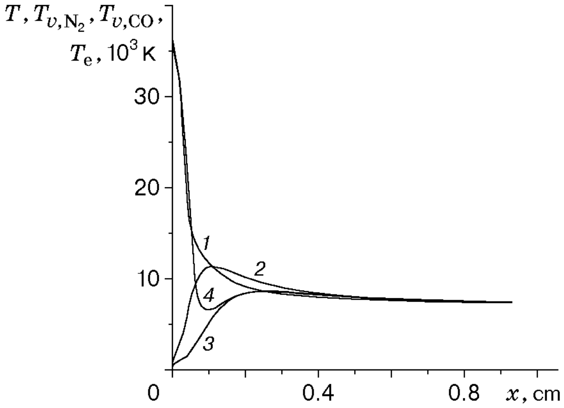

Fig. 5

quantitative data are in good agreement with the experiment (see Fig. 4). Immediately behind the shock-wave front, there is a sharp increase in the electron temperature due to the energy of the fast electrons of associative ionization. During EV exchange reactions, the electrons lose energy in excitation of the vibrational degrees of freedom of CO and N_2 molecules. The rise in the electron temperature in the quasistationary region is related to an increase in the vibrational temperature of the molecules during VT processes and redistribution of the vibrational energy of the molecules into free electrons.

A comparison of the calculated data with measurement results shows that the best agreement is provided for by a kinetic model in which, in contrast to the conventional models of [1, 2], the chosen reaction-rate constants lead to weaker dissociation of CO_2 molecules, deceleration of charge-exchange reactions with participation of C^+ ions, and slower ionization of C and O atoms by electron impact, the vibrational-dissociation interaction is described by the Kuznetsov model, the kinetics of formation of NO molecules is described by the Zel'dovich multitemperature reaction-rate constants [14], associative ionization is described by the model of [3], and the nonequilibrium distribution of the free electron temperature is taken into account. The corrected kinetic model gives a good fit to measurements of the ionization characteristics of the relaxation zone in the tested range of shock-wave speeds.

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